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(54) **Desulphurisation of oil.**

(57) A process for desulphurising hydrocarbon oils comprises the steps of (1) treating a sulphur containing hydrocarbon oil with a catalyst consisting essentially of an aqueous acidic or neutral solution of a molybdenum, tungsten or vanadium heteropolyanion and an oxidant under conditions such that the sulphur is oxidised and (2) separating the oxidised sulphur from the treated hydrocarbon oil. Preferred catalysts include those heteropolyanions derivable by ionisation of an acid having the general formula  $H_e(X_kM_nO_y)$  where X is selected from phosphorus, antimony, silicon, germanium or boron; M is selected from molybdenum, tungsten or vanadium; k is from 1 to 5; n is from 5 to 40; y is from 18 to 62 and e is the valance of the  $(X_kM_nO_y)^{e-}$  anion.

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The present invention relates to a process for oxidising sulphur derivatives useful in the removal of unwanted sulphur from sulphur containing hydrocarbon oils.

Heavy oils occur widely throughout the world and contain significant quantities of chemically bound sulphur. The presence of sulphur poses problems in that it poisons many catalytic systems employed in processes to convert heavy hydrocarbon fractions to lighter oils and gasolines. In addition, the combustion of such sulphur containing oils leads to the release of undesirable sulphur containing species known to add to atmospheric pollution.

The removal of sulphur from oils is therefore essential and processes for the removal of sulphur are known. Representative of published prior art are US 3551328, US 3565793, US 3595778, US 3816301, US 3847798 and US 3847800.

US 3551328 discloses a process for the desulphurisation of heavy hydrocarbon fractions by the oxidation of the sulphur impurities by contacting the hydrocarbon fraction with an oxidant in the presence of an oxidation promoting catalyst and further treatment with a lower paraffinic hydrocarbon solvent to separate the oxidised sulphur compounds from the hydrocarbon fraction.

US 3565793 discloses a process for the desulphurisation of hydrocarbon materials by the oxidation of the sulphur impurities and subsequent removal of the oxidised sulphur compound by thermal treatment or addition of a base.

US 3595778 discloses a desulphurisation process comprising the oxidation of the sulphur containing compounds by ozone and a vanadium catalyst followed by thermal or base treatment.

Both US 3816301 and 3847798 disclose a process for the removal of sulphur in hydrocarbons comprising oxidation of the sulphur by reacting the hydrocarbon with tertiary butyl hydroperoxide in a solvent and subsequent thermal treatment to provide a reduced sulphur content.

Finally, US 3847800 discloses a process wherein sulphur and nitrogen components are removed from petroleum oils comprising reacting the petroleum oils with a gas which includes one or more oxides of nitrogen and mixing the oxidised oil with a solvent immiscible with the oil.

A problem encountered with such processes is that the conditions are extreme and undesirable side reactions can result and catalyst recovery is normally difficult.

We have now found that sulphur levels in hydrocarbon oils can be selectively reduced under mild conditions by treating the oil with an aqueous acidic solution of a molybdenum, tungsten or vanadium heteropolyanion and an oxidant.

Accordingly the present invention comprises a process for desulphurising hydrocarbon oils comprising the steps of (1) treating a sulphur containing hydrocarbon oil with a catalyst consisting essentially of an aqueous acidic or neutral solution of a molybdenum, tungsten or vanadium heteropolyanion and an oxidant under conditions such that the sulphur is oxidised and (2) separating the oxidised sulphur from the treated hydrocarbon oil.

The present invention has the advantage that operating conditions are mild and selectivity to sulphur oxidation is high without significant amounts of unwanted side reactions.

The catalyst used to effect oxidation of the sulphur is a molybdenum, tungsten or vanadium heteropolyanion. Such species are described in detail in 'Heteropoly and Isopoly Oxo-metalates' by Pope *et al*, Springer-Verlag, New York 1983.

A preferred class of heteropolyanions for use in the process of the present invention are those derivable by ionisation of heteropolyacids having the general formula  $H_n(X_kM_nO_y)$  where X is phosphorus, antimony, silicon, germanium or boron and M is molybdenum, tungsten or vanadium. It is also preferred that k is from 1 to 5, n is from 5 to 40 and y is from 18 to 62. It will be appreciated that the value of e will equal the valence of the anion  $(X_kM_nO_y)^{e-}$  which in turn will depend upon the value of the other variables.

A particularly preferred class of heteropolyanions are those having the general formula  $(XM_{12}O_{40})^{3-}$ . Of these, the most preferred are those of formula  $(PM_{12}O_{40})^{3-}$  where M is either molybdenum or tungsten. Such species can be conveniently prepared *in situ* under the reaction conditions from either (1) the corresponding heteropolyacid  $H_3PM_{12}O_{40}$  or alkali metal or ammonium salts thereof or (2) a combination of acid, phosphate and tungstate, molybdate or vanadate salts or acids.

In general it is preferred that the volume of the aqueous catalyst phase used should be in the range 0.1 to 10 times the volume of the oil. The amount of catalyst should range from 0.0001 to 0.1 moles for every litre of water.

Whilst the oxidation can be carried out by emulsifying the oil and aqueous catalyst phase, it is preferred that oxidation is carried out in the presence of a phase transfer catalyst. Suitable phase transfer catalysts are pyridinium, quaternary ammonium or phosphonium salts, for example tricaprylmethylammonium chloride and tetraoctylammonium bromide.

The oxidants which may be used in the oxidation step include hydrogen peroxide, alkyl hydroperoxides,

eg tertiarybutylhydro peroxide, oxygen and air. The preferred oxidant is hydrogen peroxide.

The amount of oxidant required will largely be dependant on the amount of sulphur present in the oil. For hydrogen peroxide and alkyl hydroperoxides, a mole ratio of oxidant to sulphur from 0.5 to 20 is preferred. Where oxygen and air are used, pressures of up to 5MPa and 25MPa respectively are suitable.

5 After the oxidation is completed, the oxidised sulphur is separated from the treated oil. Such separation can be effected in a number of ways including solvent extraction, adsorption, pyrolysis to form sulphur monoxide and/or sulphur dioxide, acid hydrolysis and precipitation. One preferred method however is to contact the treated hydrocarbon oil with an immiscible solvent. Preferred solvents include C<sub>1</sub> to C<sub>4</sub> alcohol and C<sub>1</sub> to C<sub>4</sub> alcohol/water mixtures, examples of which are methanol or methanol/water. The amount of immiscible solvent  
10 used is typically in the range 0.5 to 10 times the volume of hydrocarbon oil being treated.

Another preferred method is adsorption of the sulphur on an active material such as alumina silica charcoal or the like. This can be achieved by, for example, passing the hydrocarbon oil through a bed or column of the material onto which absorption occurs.

Finally under some circumstances it may be preferred to effect the separation by distillation using for  
15 example the method quoted in ASTM D 2892.

The present invention is now further illustrated with reference to the following examples.

#### Example 1

20 A round bottom flask fitted with a condenser was charged with H<sub>2</sub>O<sub>2</sub>(23.5mmol), a light gas oil (10.02g), tricaprylylmethylammonium chloride (0.2mmol) and 4cm<sup>3</sup> of an aqueous solution of phosphotungstic acid H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> (0.035g, 0.012mmol). The contents of the flask were heated with stirring to 60°C and the temperature maintained for 1.5 hours. The vessel was cooled and an orange oil was observed to precipitate out of solution. The orange oil was separated from the light gas oil and the latter washed with methanol (25cm<sup>3</sup>). Sulphur  
25 content in the light gas oil was determined by x-ray fluorescence and found to be 1.3% w/w prior to treatment, 1.09% w/w after treatment but unwashed and 0.27% w/w after washing with methanol.

#### Comparative Example 1

30 A round bottom flask fitted with a condenser was charged with H<sub>2</sub>O<sub>2</sub>(23.5mmol), a light gas oil (10g), tricaprylylmethylammonium chloride (0.2mmol) and 4 cm<sup>3</sup> of water. The contents of the flask were heated with stirring to 60°C and the temperature maintained for 1.5 hours. A precipitate was not observed on cooling.

#### Example 2

35 Hydrogen Peroxide as Oxidant

In a typical run H<sub>2</sub>O<sub>2</sub> (16.8 mmol; 19% by volume) was added to diesel (20.0g, 0.253% wt S) containing tricaprylylammonium chloride (0.25 mmol). To this was added 7.5 cm<sup>3</sup> of an aqueous solution of phosphomolybdic acid (0.022 mmol). The reaction mixture was heated to 60°C for 2.5h. A small amount of a dark brown oil was observed to precipitate from solution whilst the diesel became dark brown-orange in colour. The diesel phase was extracted with methanol (2 x 25 cm<sup>3</sup> portions) the latter assuming an orange/brown colouration. The % sulphur content of the extracted diesel (determined by XRF) was found to be 0.097%.

#### Example 3

45 In a typical run H<sub>2</sub>O<sub>2</sub> (16.8 mmol; 19% by volume) was added to diesel (20.0g, 0.253% wt S) containing tricaprylylammonium chloride (0.25 mmol). To this was added 7.5 cm<sup>3</sup> of an aqueous solution of phosphotungstic acid (0.01 mmol). The reaction mixture was heated to 60°C for 2.5h. A small amount of a dark brown oil precipitated from solution whilst the diesel became dark brown/orange in colour. The diesel was extracted with methanol as described in Example 1. The %S content of the extracted diesel was found to be 0.085 % wt.

#### Example 4

55 In a typical run H<sub>2</sub>O<sub>2</sub> (11.96 mmol, 19% by volume) was added to a diesel (20.1 g, 0.253 % wt S) containing tricaprylylammonium chloride (0.124 mmol). To this was added methanol (10.15 g) and phosphomolybdic acid H<sub>3</sub>PMO<sub>12</sub>O<sub>40</sub> (0.022 mmol). The reaction mixture was heated to 60°C for 2.5h. The methanol phase assumed a dark green/brown colouration but on cooling turned dark orange-brown in colour. The diesel was separated

and then extracted with a further 25 cm<sup>3</sup> of methanol. The % S content of the extracted diesel was found to be 0.076 % wt.

#### Example 5

In a typical run H<sub>2</sub>O<sub>2</sub> (6.38 mmol, 19% by volume) was added to diesel (9.9g) containing tricaprylylammonium chloride (0.124 mmol). To this was added 10.0g of an aqueous solution of phosphotungstic acid (0.03 mmol). The reaction mixture was heated to 60°C for 1.5h. The aqueous phase was separated and this together with H<sub>2</sub>O<sub>2</sub> (14.25 mmol, 19% by volume) was added to diesel (20.1g, 0.253% wt S) containing aliquat 336 (0.124 mmol). The reaction mixture was heated to 60°C for 2 h. A brown oil precipitated from solution and the diesel phase was extracted with methanol as described in Example 1. The % S content of the extracted diesel was 0.085% wt.

#### Example 6

##### Oxidation of Straight Run Gas Oil

A two-litre glass reactor was charged with 776.8g of a diesel oil (UK winter grade from BP's Grangemouth Refinery, no ignition improver, consisting essentially of straight run non-hydrotreated gas oil, 0.253 wt. % sulphur), phosphotungstic acid (2.5g in 15g water), 'Aliquat 336' (tri-n-octylmethylammonium chloride, 4.15g), and a solution of H<sub>2</sub>O<sub>2</sub> (49.8g 100%) in 388.9g H<sub>2</sub>O. The contents were heated to 60°C and stirred at that temperature for 4 hours, then cooled to 20°C. The bulk diesel phase was separated from the aqueous phase and a small precipitate of a dark brown oil (5g). XRF analysis showed the bulk phase and the precipitate to contain 0.255 and 1.87 wt % sulphur respectively.

#### Example 7

##### Pyrolysis of Oxidised Straight Run Gas Oil

A 187.8g sample of diesel oxidised as described in Example 6 was charged to a 600 cm<sup>3</sup> stainless steel Baskerville autoclave which was then capped, leak tested with N<sub>2</sub> at 45 bar and then vented to 0 bar gauge and sealed. The contents were stirred at 250 rpm, heated to 400°C over 1½ h and kept at 400-410°C for one hour. After slow cooling overnight to ambient temperature, the final pressure was 1.0 bar gauge. Nitrogen gas was added to 5 bar gauge and the gases then released through a NaOH (aq) scrubber. The vessel was pressured to 45 bar with N<sub>2</sub> and then slowly vented. On opening the vessel a revolting odour was apparent. The liquors were collected (182.3g) leaving a small amount of a carbonaceous residue and degassed for 15 mins with a stream of N<sub>2</sub>. Analysis by XRF showed the presence of 0.177 wt % sulphur.

#### Example 8

##### Absorption of Oxidised Straight Run Gas Oil

A glass column (1x30cm) was filled with silica (5g) that had been dried at 160°C in a vacuum oven overnight. The oxidised diesel of Example 6 (75g) was then loaded onto the column and fractions (2g) of the effluent collected. The column was run under a slight nitrogen pressure to achieve a flow rate of about 25g/h. After all the diesel had loaded, 33 fractions had been collected. A further 2.7g was collected by allowing the column to run to dryness under nitrogen pressure. This implies that 6.3g of diesel remained entrained in the pores of the silica. The results obtained are given in Table 1.

TABLE 1SULPHUR CONCENTRATION IN FRACTIONS COLLECTED FROM SILICA COLUMN

Fraction No	%wt-S	Fraction No	%wt-S	Fraction No	%wt-S
1	0.002	12	0.005	23	0.009
2	0.007	13	0.005	24	0.011
3	0.005	14	0.006	25	0.016
4	0.006	15	0.006	26	0.024
5	0.005	16	0.005	27	0.034
6	0.005	17	0.005	28	0.050
7	0.006	18	0.005	29	0.068
8	0.005	19	0.005	30	0.092
9	0.005	20	0.005	31	0.107
10	0.005	21	0.006	32	0.124
11	0.006	22	0.007	33	0.140

Example 9Distillation of Oxidised Straight Run Gas Oil

Distillation was carried out using a column packed with stainless steel gauze (Propak) giving an efficiency of about 15 theoretical plates. The method was essentially as described in ASTM D2892 although smaller scale equipment was used.

Distillation of the product of Example 6 gave results shown in Table 2.

TABLE 2DISTILLATION OF STRAIGHT RUN GAS OIL

Fraction (°C)	Gas Oil		Oxidised Gas Oil	
	Yield (%wt)	Sulphur (%wt)	Yield (%wt)	Sulphur (%wt)
IBP - 210	14.10	0.025	14.25	0.005
210 - 300	46.15	0.187	43.75	0.041
300 - 330	18.60	0.319	19.0	0.18
330 - 342	6.45	0.460	7.05	0.25
>342 (residue)	14.50	0.497	15.35	0.86
Loss	0.20		0.60	
<u>Totalised</u>				
IBP - 210	14.10	0.025	14.25	0.005
IBP - 300	60.25	0.149	58.0	0.032
IBP - 330	78.85	0.189	77.0	0.069
IBP - 342	85.30	0.210	84.05	0.084

Claims

1. A process for desulphurising hydrocarbon oils comprising the steps of (1) treating sulphur containing oil with a catalyst consisting essentially of an aqueous acidic or neutral solution of a molybdenum, tungsten or vanadium heteropolyanion and an oxidant under conditions such that the sulphur is oxidised and (2) separating the oxidised sulphur from the treated hydrocarbon oil.
2. A process as claimed in claim 1 wherein the molybdenum, tungsten or vanadium heteropolyanion is derivable by ionisation of a heteropolyacid having the general formula  $H_n(X_kM_nO_y)$  where X is selected from phosphorus, antimony, silicon, germanium or boron; M is selected from molybdenum, tungsten or vanadium; k is from 1 to 5; n is from 5 to 40; y is from 18 to 62 and e is the valance of the  $(X_kM_nO_y)^{e-}$  anion.
3. A process as claimed in claim 2 wherein the heteropolyacid has the general formula  $H_3XM_{12}O_{40}$  where M is either molybdenum or tungsten.
4. A process as claimed in claim 3 wherein X is phosphorus.
5. A process as claimed in claim 1 wherein the molybdenum, tungsten or vanadium heteropolyanion is generated in situ under the reaction conditions from the corresponding alkali metal or ammonium salt or the corresponding heteropolyacid.
6. A process as claimed in claim 1 wherein step (1) is carried out in the presence of a phase transfer catalyst which is a quaternary ammonium or phosphonium salt.
7. A process as claimed in claim 1 wherein step (2) comprises treating the treated oil with an immiscible solvent comprising a  $C_1$  to  $C_4$  alcohol or a mixture of a  $C_1$  to  $C_4$  alcohol and water.
8. A process as claimed in claim 1 wherein the sulphur containing hydrocarbon oil, catalyst and oxidant are employed as an emulsion.



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number

EP 91 30 9649

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US-A-4 156 641 (UOP)		C10G27/04
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A	US-A-3 825 488 (UOP)		
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A	US-A-3 813 329 (UOP)		
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A	EP-A-0 031 729 (DU PONT DE NEMOURS)		
	---		
A	EP-A-0 064 371 (SUMIMOTO CHEMICAL COMPANY)		
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			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C10G B01J
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 28 JANUARY 1992	Examiner MICHIELS P.
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